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TI High-strength **magnesium alloys**
IN Kubota, Kohei; Ninomya, Ryuji; Gyuntaa, Naite; Ebahaado, Ii Shumitsuto
PA Mitsui Mining & Smelting Co, Japan; Metallgesellschaft Ag
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AB The **Mg alloys** contain lanthanoid 0.5-5, **Ca** 0.5-5, and **Mn** ≤1.5 and/or Zr ≤1.5%, and optionally Ag 0.5-4%. Alternatively, the **Mg alloys** contain lanthanoid 0.5-5, **Ca** 0.5-5, **Mn** ≤1.5, and Al 1-9.5 or Zn 1-7.5%. The **Mg alloys** may contain Yt ≤5.5, **Sr** ≤1.5, and/or Sc ≤10%. (Die) casting parts manufactured from the **Mg alloys** are also claimed. The **Mg alloys** show high strength at room and high temperature, and are useful for automobile engine parts.

1-9.5 Al
≤1.5 Mn
Zn
0.5-5 Ca
≤1.5 Sr
0.5-5 REM
Mag

1-2.5

PATENT ABSTRACTS OF JAPAN

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(54) HIGH STRENGTH MAGNESIUM ALLOY

(57)Abstract:

PURPOSE: To obtain a general purpose heat resistant lightweight magnesium alloy having room temp. and high temp. strengths more excellent than those of various lanthanoid-contg. magnesium alloys for high temp. use which have been practically used heretofore and suitable for automotive engine parts requiring lightness and heat resistance.

CONSTITUTION: This magnesium ally has a compsn. contg. (A) 0.5 to 5 wt.% lanthanoid, (B) 0.5 to 5 wt.% calcium and (C) either or both of ≤1.5 wt.% manganese and ≤1.5 wt.% zirconium, contg. (D) one kind selected from a group composed of 1 to 9.5 wt.% aluminum, 1 to 7.5 wt.% zinc and 0.5 to 4 wt.% silver at request, furthermore contg. (E) at least one kind selected from the group consisting of ≤5.5 wt.% yttrium, ≤1.5 wt.% strontium and ≤10 wt.% scandium at request, and the balance magnesium with inevitable impurities.

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CLAIMS

[Claim(s)]
[Claim 1] (b) 0.5 - 5 % of the weight of lanthanoidses, and (**) -- a Magnesium alloy excellent in a room temperature and high temperature strength which are characterized by containing 0.5 - 5 % of the weight of calcium (Ha), 1.5 or less % of the weight of manganese, and 1.5 or less % of the weight of both both [either or], and the remainder consisting of magnesium and an unescapable impurity.
[Claim 2] (b) 1 - 9.5 % of the weight of aluminum, and (**) -- a Magnesium alloy excellent in a room temperature and high temperature strength which are characterized by containing 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, and 1.5 or less % of the weight of (d) manganese, and the remainder consisting of magnesium and an unescapable impurity.
[Claim 3] (b) 1 - 7.5 % of the weight of zinc, and (**) -- a Magnesium alloy excellent in a room temperature and high temperature strength which are characterized by containing 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, and 1.5 or less % of the weight of (d) manganese, and the remainder consisting of magnesium and an unescapable impurity.
[Claim 4] (b) 0.5 - 4 % of the weight of silver, and (**) -- a Magnesium alloy excellent in a room temperature and high temperature strength which are characterized by containing 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, 1.5 or less % of the weight of (d) manganese, and 1.5 or less % of the weight of both both [either or], and the remainder consisting of magnesium and an unescapable impurity.
[Claim 5] A Magnesium alloy excellent in a room temperature and high temperature strength given in any of claims 1-4 they are which contain further at least one sort chosen from a group which consists of 5.5 or less % of the weight of yttriums, 1.5 or less % of the weight of strontium, and 10 or less % of the weight of scandiums.
[Claim 6] Casting and die-casting components which consist of an alloy given in any of claims 1-5 they are.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the Magnesium alloy which has reinforcement sufficient also at the elevated temperature to about [which is demanded in lightweight-izing of automobile engine components etc. in more detail] 523K about the Magnesium alloy excellent in a room temperature and high temperature strength.
[0002]
[Description of the Prior Art] The request of the improvement in fuel consumption of an automobile becomes strong, and development of the charge for automobiles of lighter weight materials has become asking strongly from the rise of the consciousness of earth environmental protection in recent years.
[0003] In the metallic material by which current utilization is carried out, a Magnesium alloy is low density most and is strongly expected as a future charge for automobiles of lighter weight materials. Current and the Magnesium alloy most generally used are Mg-aluminum-Zn-Mn system alloys (for example, AZ91 alloy =Mg-9aluminum-1Zn-0.5Mn), circumference technology, such as foundry technique of this alloy, is in a completion phase, and this alloy is first examined in the formation of automobile lightweight. Moreover, the alloy which added the lanthanoids (Ln) with magnesium as a Magnesium alloy for heatproofs is developed. As such an alloy, there are a Mg-Ln-Zr system alloy, a Mg-aluminum-Ln-Zr system alloy (refer to JP,46-6202,A), a Mg-Zn-Ln-Zr system alloy (refer to JP,52-92811,A), and a Mg-Ag-Ln-Zr system alloy (refer to each official report of JP,51-92707,A, JP,51-92708,A, and JP,52-101615,A). Furthermore, the Mg-Y-Nd-Zr system alloy (refer to JP,57-210946,A) is developed.
[0004]
[Problem(s) to be Solved by the Invention] However, the above-mentioned Mg-aluminum-Zn-Mn system alloy does not fit the use as which reinforcement falls or more by 393K, and thermal resistance is required also in automobile engine components. Moreover, Zr used as an indispensable component for detailed-izing of the method which there is an inclination for Ln to incline toward the lower part in a molten metal since Ln is a heavy element in Ln content alloys, such as the above-

mentioned heat-resistant Mg-Ln-Zr system, then controls the amount of Ln(s) as much as possible, and cast structure has an unstable addition yield, and since it becomes cost high, the method of controlling an addition, using the alternative element of Zr is searched for. Furthermore, 4% of the weight or more, since Nd is contained 3% of the weight or more, it is hard to use expensive Y for mass production, such as an automobile, with the above-mentioned Mg-Y-Nd-Zr system alloy developed for the thermal resistance of alloys, such as such a Mg-Ln-Zr system, being inadequate in cost.

[0005] This invention is made in view of the technical problem which such conventional technology has, and the object of this invention is to offer the new heat-resistant high intensity Magnesium alloy suitable for the charge of automobile engine components lumber as which both thermal resistance and room temperature reinforcement are required.

[0006]

[Means for Solving the Problem] Since this invention person etc. had an effect also in detailed-ization of cast structure when a room temperature and high temperature strength improved further and were able to control an amount of Ln by replacing with Ln added by high-temperature-service Magnesium alloy as a result of repeating examination variously, in order to solve the above-mentioned technical problem, and using Ln+calcium, it found out that an amount of Zr could also be controlled. Moreover, a room temperature and high temperature strength reached [improving further and] a header and this invention by adding further at least one sort chosen from a group which consists of Y, Sr, and Sc by request.

[0007] namely, a Magnesium alloy excellent in a room temperature and high temperature strength of this invention -- (**) -- 0.5 - 5 % of the weight of lanthanoidses, and (**) -- 0.5 - 5 % of the weight of calcium (Ha), 1.5 or less % of the weight of manganese, and 1.5 or less % of the weight of both both [either or] are contained, and it is characterized by the remainder consisting of magnesium and an unescapable impurity.

[0008] moreover, a Magnesium alloy excellent in a room temperature and high temperature strength of this invention -- (**) -- 1 - 9.5 % of the weight of aluminum, and (**) -- 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, and 1.5 or less % of the weight of (d) manganese are contained, and it is characterized by the remainder consisting of magnesium and an unescapable impurity.

[0009] furthermore, a Magnesium alloy excellent in a room temperature and high temperature strength of this invention -- (**) -- 1 - 7.5 % of the weight of zinc, and (**) -- 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, and 1.5 or less % of the weight of (d) manganese are contained, and it is characterized by the remainder consisting of magnesium and an unescapable impurity.

[0010] furthermore, a Magnesium alloy which was excellent in a room temperature and high temperature strength of this invention again -- (**) -- 0.5 - 4 % of the weight of silver, and (**) -- 0.5 - 5 % of the weight of lanthanoidses, 0.5 - 5 % of the weight (Ha) of calcium, 1.5 or less % of the weight of (d) manganese, and 1.5 or less % of the weight of both both [either or] are contained, and it is

characterized by the remainder consisting of magnesium and an unescapable impurity.

[0011] A Magnesium alloy excellent in a room temperature and high temperature strength of this invention can contain further at least one sort further chosen from a group which consists of 5.5 or less % of the weight of yttriums, 1.5 or less % of the weight of strontium, and 10 or less % of the weight of scandiums much more preferably.

[0012] Moreover, this invention relates also to casting and die-casting components which consist of an alloy given in above any they are.

[0013] Although there are Mg system, a Mg-aluminum system, a Mg-Zn system, and a Mg-Ag system as a Magnesium alloy, in an alloy of each system, an addition of aluminum, zinc, or silver is mostly established as an amount dissolution and precipitation strengthening are accepted to be.

[0014] In a Magnesium alloy of this invention in a case of adding aluminum, aluminum dissolves with magnesium, shows age-hardening nature, and raises a mechanical property of an alloy. Although the addition effect of aluminum increases with an increment in the addition, less than 1 % of the weight is insufficient, and saturation is reached at 9.5 % of the weight. Furthermore, elongation of an alloy falls as an addition of aluminum increases. Therefore, in a Magnesium alloy of this invention, in adding aluminum, it makes an aluminum addition into 3 - 7 % of the weight preferably one to 9.5% of the weight.

[0015] In a Magnesium alloy of this invention in a case of adding zinc, zinc is an element effective in improvement in room temperature reinforcement. However, when a zincky addition is less than 1 % of the weight, reinforcement of a Mg-aluminum system alloy is not filled with room temperature reinforcement of the alloy, but it is inadequate. Moreover, although room temperature reinforcement improves with an increment in the amount of zincings, when the addition effect reaches saturation at the 7.5 % of the weight of the amounts of zincings and is added exceeding 7.5 % of the weight, the ductility of an alloy will decrease. Therefore, in a Magnesium alloy of this invention, in adding zinc, it makes the amount of zincings into 3 - 7 % of the weight preferably one to 7.5% of the weight.

[0016] In a Magnesium alloy of this invention in a case of adding silver, contributing silver to the thermal resistance of an alloy and improvement in on the strength is known. However, the addition effect is not attained when a silver addition is less than 0.5 % of the weight. Although the thermal resistance of an alloy and reinforcement increase with an increment in a silver addition, an effect over buildup of alloy reinforcement is saturated with 4 % of the weight, and even if it adds more than it, buildup of alloy reinforcement beyond it is not accepted. On the other hand, when it adds exceeding 4 % of the weight, an alloy becomes weak and processability will also fall. Therefore, in a Magnesium alloy of this invention, in adding silver, it makes a silver addition into 1.5 - 3.5 % of the weight preferably 0.5 to 4% of the weight.

[0017] A lanthanoids (for example, neodymium, a lanthanum, a cerium, a misch metal) of raising high temperature strength of a Magnesium alloy is well-known, and neodymium is used for a Magnesium alloy for heatproofs especially recently. Calcium is also an element effective in improvement in high temperature strength of a Magnesium alloy. When an addition of a lanthanoids and calcium is less than 0.5 % of the weight, high temperature strength of the alloy is [in / both / a Magnesium alloy of

this invention] inadequate. When both additions of a lanthanoids and calcium are 0.5 - 5 % of the weight, a room temperature and high temperature strength become very high rather than a case where a lanthanoids or calcium of an amount equal to the total quantity is added, namely, the synergistic effect is attained. Moreover, a room temperature and high temperature strength improve further with a comparatively small lanthanoids addition by replacing a part of lanthanoids from calcium, and further, since calcium is a light element, an inclination of gravity segregation of a lanthanoids is mitigated by this substitute. If an addition of a lanthanoids or calcium exceeds 5 % of the weight, each addition limit will be arrived at, the amount of crystallization of an intermetallic compound of the grain boundary increases, and an alloy embrittles. Therefore, in a Magnesium alloy of this invention, an addition of calcium is preferably made into 0.5 - 3 % of the weight for an addition of a lanthanoids 0.5 to 5% of the weight one to 4% of the weight 0.5 to 5% of the weight.

[0018] As detailed-ized material of crystal grain of a Magnesium alloy, conventionally, although it is known by Mg-aluminum system alloy that manganese of a zirconium is the most effective in Mg system, a Mg-Zn system, and a Mg-Ag system light alloy again, since there is an effect also in detailed-ization of cast structure according to concomitant use about a lanthanoids and calcium, in a Magnesium alloy of this invention, the whole quantity or a part of zirconium can be transposed to it from manganese. In a Magnesium alloy of this invention, each addition of a ** zirconium which attains an effect of making an organization detailed and raising reinforcement, and manganese is 1.5 or less % of the weight.

[0019] All of an yttrium, strontium, and a scandium are elements effective in improvement in high temperature strength of a Magnesium alloy. However, in a Magnesium alloy of this invention, by using together these yttriums, strontium, or a scandium with lanthanoids + calcium, a room temperature and high temperature strength become very high rather than a case where a lanthanoids, calcium, an yttrium, strontium, or a scandium of an amount equal to the total quantity is added, namely, the synergistic effect is attained. However, if 5.5 % of the weight of additions of an yttrium, 1.5 % of the weight of additions of strontium, and 10 % of the weight of additions of a scandium are exceeded, each addition limit will be arrived at, the amount of crystallization of an intermetallic compound of the grain boundary increases, and an alloy embrittles. Therefore, in a Magnesium alloy of this invention, in adding an yttrium, strontium, or a scandium, it makes [an addition of an yttrium] an addition of a scandium into 1 - 5 % of the weight for an addition of strontium 10 or less % of the weight 0.5 to 1% of the weight 1.5 or less % of the weight one to 5% of the weight preferably 5.5 or less % of the weight.

[0020]

[Example]

Raw material was inserted in and it was made to dissolve in the vacuum melting furnace of examples 1-13 and the example 1 of a comparison - 11 argon ambient atmosphere so that it may become the alloy of the presentation shown in a table 1. In addition, using a misch metal as a lanthanoids, SUS304 material was used as crucible and flux etc. was not used. The molten metal was cast in 25mmx50mmx300mm metal mold, and the casting for a trial was created. Thus, the JIS No. 4 test

piece was created from the obtained casting for a trial. In addition, each heat treatment is 500 K or 10 hours. :tension test which carried out the following trials using these test pieces: Measure by elongation =% with the Instron tension tester at the time of measurement-unit =MPa of crosshead speed 10 mm/min, the measurement temperature 298K and 523K, and tensile strength, and fracture. The measurement result was as being shown in a table 1 (% in a table is elongation at the time of fracture).

[0021]

[A table 1]

	合金組成					298K		523K	
例番号	Mm	Ca	Mn	Mg	その他	引張強度	%	引張強度	%
比較例1 (TK41)	4.0	—	—	残	Zr:0.7	230	3	120	8
比較例2	—	4.0	0.5	残	—	235	3	130	6
実施例1	2.0	2.0	0.5	残	—	263	3	145	8
実施例2	4.0	1.0	—	残	Zr:0.2	262	3	142	7
実施例3	1.0	4.0	0.5	残	—	260	3	145	5
比較例3	5.5	0.3	—	残	Zr:0.7	185	1	135	5
比較例4	0.3	5.5	0.7	残	—	170	〈1	130	5
実施例4	2.0	2.0	0.5	残	Y:2.0	292	3	165	6
実施例5	2.0	2.0	0.5	残	Sr:1.0	285	4	148	7
実施例6	2.0	2.0	0.5	残	Sc:2.0	295	3	166	6
比較例5	2.0	2.0	0.5	残	Y:6.0	195	1	140	3
比較例6 (AE42)	2.0	—	0.7	残	Al:4.0	245	3	105	5
実施例7	1.0	1.0	0.5	残	Al:4.0	275	3	125	5
実施例8	1.0	1.0	0.5	残	Al:4.0 Y:1.0	305	3	140	5
比較例7	1.0	1.0	0.5	残	Al:10.0	280	1	100	3
比較例8 (ZT42)	2.0	—	—	残	Zn:4.0 Zr:3.5	230	3	115	5
実施例9	1.0	1.0	0.5	残	Zn:4.0	275	3	135	5
実施例10	1.0	1.0	0.3	残	Zn:4.0 Sr:0.08	290	3	140	5
比較例9	1.0	1.0	0.5	残	Zn:9.0	270	1	102	2
比較例10 (QE22)	2.0	—	—	残	Ag:2.5 Zr:0.7	240	3	130	5
実施例11	1.0	1.0	0.5	残	Ag:2.5	305	3	150	5
実施例12	1.0	1.0	0.2	残	Ag:1.8 Y:1.0	295	3	170	5
実施例13	1.0	1.0	0.2	残	Ag:2.5 Sc:1.0	290	4	165	6
比較例11	1.0	1.0	0.2	残	Ag:5.0	295	1	140	3

[0022] When improvement remarkable about both room temperature reinforcement and high temperature strength is found when equivalent misch metal + calcium replaces a misch metal and an

yttrium, strontium, or a scandium is further added to this so that clearly from above-mentioned examples 1-13 and examples 1-11 of a comparison, it is alike about both room temperature reinforcement and high temperature strength, and still more remarkable improvement is found. Although it is the alloying element which raises room temperature reinforcement and high temperature strength as for all of a lanthanoids, calcium, an yttrium, strontium, and a scandium although not solved still clearly about this reason, since that mechanism, especially crystallization differ from the class of intermetallic compound which deposits, what is depended on the addition effect attaining a tatami weight and the synergistic effect, and attaining the effect which controls the required element addition itself mutually and suits is conjectured.

[0023] Moreover, also when the zirconium made indispensable in the lanthanoids content Magnesium alloy is transposed to manganese, it turns out that the detailed-ized effect by big and rough-ized private seal **** of the crystalline structure and lanthanoids + calcium is effective.

[0024] Furthermore, when each alloying element is added more than a constant rate so that clearly from the examples 1-11 of a comparison, the alloy will embrittle, and some of room temperature reinforcement, high temperature strength, elongation, or all will fall, or the addition effect will be saturated. Detailed-ization of the improvement in on the strength and the organization by dissolution, crystallization, and deposit can be attained on the level from which an intermetallic compound crystallizes the reason slightly, and in addition beyond it, there are too many amounts of crystallization of an intermetallic compound, and it is for embrittling a grain boundary.

[0025]

[Effect of the Invention] The Magnesium alloy of this invention is a general-purpose heat-resistant lightweight Magnesium alloy suitable for the automobile engine components with which various kinds of lanthanoids content Magnesium alloys of the high temperature service currently used conventionally are excelled in a room temperature and high temperature strength, and a light weight and thermal resistance are demanded.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the Magnesium alloy which has reinforcement sufficient also at the elevated temperature to about [which is demanded in lightweight-izing of automobile engine components etc. in more detail] 523K about the Magnesium alloy excellent in a room temperature and high temperature strength.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] The Magnesium alloy of this invention is a general-purpose heat-resistant lightweight Magnesium alloy suitable for the automobile engine components with which various kinds of lanthanoids content Magnesium alloys of the high temperature service currently used conventionally are excelled in a room temperature and high temperature strength, and a light weight and thermal resistance are demanded.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, the above-mentioned Mg-aluminum-Zn-Mn system alloy does not fit the use as which reinforcement falls or more by 393K, and thermal resistance is required also in automobile engine components. Moreover, Zr used as an indispensable component for detailed-izing of the method which there is an inclination for Ln to incline toward the lower part in a molten metal since Ln is a heavy element in Ln content alloys, such as the above-mentioned heat-resistant Mg-Ln-Zr system, then controls the amount of Ln(s) as much as possible, and cast structure has an unstable addition yield, and since it becomes cost high, the method of controlling an addition, using the alternative element of Zr is searched for. Furthermore, 4% of the weight or more, since Nd is contained 3% of the weight or more, it is hard to use expensive Y for mass production, such as an automobile, with the above-mentioned Mg-Y-Nd-Zr system alloy developed for the thermal resistance of alloys, such as such a Mg-Ln-Zr system, being inadequate in cost.
[0005] This invention is made in view of the technical problem which such conventional technology has, and the object of this invention is to offer the new heat-resistant high intensity Magnesium alloy suitable for the charge of automobile engine components lumber as which both thermal resistance and room temperature reinforcement are required.

[Translation done.]

EXAMPLE

[Example]
Raw material was inserted in and it was made to dissolve in the vacuum melting furnace of examples 1-13 and the example 1 of a comparison - 11 argon ambient atmosphere so that it may become the alloy of the presentation shown in a table 1. In addition, using a misch metal as a lanthanoids, SUS304 material was used as crucible and flux etc. was not used. The molten metal was cast in 25mmx50mmx300mm metal mold, and the casting for a trial was created. Thus, the JIS No. 4 test piece was created from the obtained casting for a trial. In addition, each heat treatment is 500 K or 10 hours. :tension test which carried out the following trials using these test pieces: Measure by elongation =% with the Instron tension tester at the time of measurement-unit =MPa of crosshead speed 10 mm/min, the measurement temperature 298K and 523K, and tensile strength, and fracture. The measurement result was as being shown in a table 1 (% in a table is elongation at the time of fracture).
[0021]
[A table 1]

	合金組成					298K		523K	
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実施例5	2.0	2.0	0.5	残	Sr:1.0	285	4	148	7
実施例6	2.0	2.0	0.5	残	Sc:2.0	295	3	166	6
比較例5	2.0	2.0	0.5	残	Y:6.0	195	1	140	3
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比較例9	1.0	1.0	0.5	残	Zn:9.0	270	1	102	2
比較例10 (QE22)	2.0	—	—	残	Ag:2.5 Zr:0.7	240	3	130	5
実施例11	1.0	1.0	0.5	残	Ag:2.5	305	3	150	5
実施例12	1.0	1.0	0.2	残	Ag:1.8 Y:1.0	295	3	170	5
実施例13	1.0	1.0	0.2	残	Ag:2.5 Sc:1.0	290	4	165	6
比較例11	1.0	1.0	0.2	残	Ag:5.0	295	1	140	3

[0022] When improvement remarkable about both room temperature reinforcement and high temperature strength is found when equivalent misch metal + calcium replaces a misch metal and an yttrium, strontium, or a scandium is further added to this so that clearly from above-mentioned examples 1-13 and examples 1-11 of a comparison, it is alike about both room temperature reinforcement and high temperature strength, and still more remarkable improvement is found. Although it is the alloying element which raises room temperature reinforcement and high temperature strength as for all of a lanthanoids, calcium, an yttrium, strontium, and a scandium although not solved still clearly about this reason, since that mechanism, especially crystallization differ from the class of intermetallic compound which deposits, what is depended on the addition effect attaining a tatami weight and the synergistic effect, and attaining the effect which controls the

required element addition itself mutually and suits is conjectured.

[0023] Moreover, also when the zirconium made indispensable in the lanthanoids content Magnesium alloy is transposed to manganese, it turns out that the detailed-ized effect by big and rough-ized private seal **** of the crystalline structure and lanthanoids + calcium is effective.

[0024] Furthermore, when each alloying element is added more than a constant rate so that clearly from the examples 1-11 of a comparison, the alloy will embrittle, and some of room temperature reinforcement, high temperature strength, elongation, or all will fall, or the addition effect will be saturated. Detailed-ization of the improvement in on the strength and the organization by dissolution, crystallization, and deposit can be attained on the level from which an intermetallic compound crystallizes the reason slightly, and in addition beyond it, there are too many amounts of crystallization of an intermetallic compound, and it is for embrittling a grain boundary.

[Translation done.]